Macromolecular Reaction Engineering
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Propagation Kinetics of Isoprene Radical Homopolymerization Derived from Pulsed Laser Initiated Polymerizations

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The propagation kinetics of isoprene radical polymerizations in bulk and in solution are investigated via pulsed laser initiated polymerizations and subsequent polymer analyses via size-exclusion chromatography, the PLP-SEC method. Because of low polymerization rate and high volatility of isoprene, the polymerizations are carried out at elevated pressure ranging from 134 to 1320 bar. The temperatures are varied between 55 and 105 °C. PLP-SEC yields activation parameters of k_p (Arrhenius parameters and activation volume) over a wide temperature and pressure range that allow for the calculation of k_p at technically relevant ambient pressure conditions. The k_p values determined are very low, e.g., 99 L mol^{-1} s^{-1} at 50 °C, which is even lower than the corresponding value for styrene polymerizations. The presence of a polar solvent results in a slight increase of k_p compared to the bulk system. The k_p values reported are important for determining rate coefficients of other elemental reactions from coupled parameters as well as for modeling isoprene free-radical polymerizations and reversible deactivation radical polymerization with respect to tailored polymer properties and optimizing the polymerization processes.

1. Introduction

Isoprene-based elastomers are of great interest for high performance synthetic rubbers. Isoprene (IP) polymerizations may lead to various configurations in the polymer, which, for example, affects crystallinity and the glass transition temperature, T_G, of the material. Another way of affecting T_G is to copolymerize IP with a polar monomer, e.g., such as glycidyl methacrylate (GMA).[1,2] Moreover, complex copolymer structures such as di-, tri-, and multiblock copolymers are considered, for example, because of their phase behavior and mechanical properties.[3]

While so far mostly anionic and coordination polymerizations of isoprene were performed, recently, there are reports on radical polymerizations of isoprene, because the latter are known to be robust and comparably easy to perform. In particular, reversible deactivation radical polymerization techniques have been applied to isoprene homo- and copolymerizations.[4–6] Copolymerizations of isoprene with polar monomers are reported to be attractive with respect to technical applications, for example, such as compatibilizers, impact modifiers, and adhesives, since the compatibility with polar substrates is improved.[6] Despite technical importance and the interest in developing novel materials, literature reports on the kinetics of isoprene (IP) radical polymerizations are still scarce. To the best of our knowledge, Morton et al. provided the only propagation rate coefficients, k_p, for isoprene: a k_p value of 2.8 L mol^{-1} s^{-1} at 5 °C.[7] Just recently, copolymerization propagation rate coefficients, k_{pcopo}, for the GMA–IP systems were determined.[8] However, k_p for IP homopolymerization and for copolymerization with high IP contents was not accessible.

The copolymerization GMA–IP propagation rate coefficients were determined using pulsed-laser initiated polymerization (PLP) and subsequent polymer analyses via size-exclusion chromatography (SEC). The so-called PLP-SEC technique introduced by Olaj et al.[9] is the method of choice for the determination of reliable propagation rate coefficients as suggested by an IUPAC Polymer Division Working Party.[10] The PLP-SEC method allows for the determination of k_p according to Equation (1)

$$k_p = \frac{L}{c_M \cdot t} \quad (1)$$

with the monomer concentration, c_M, the time between subsequent laser pulses, t, and the characteristic chain length L. As outlined in the original work by Olaj, mostly L is best represented by the chain length derived from the molar mass at the first inflection point of the molar mass distribution.[9] Equation (1) shows that the PLP-SEC method does not depend on the knowledge of the radical concentration. Applying PLP-SEC benchmark k_p values were published for a number of acrylates, methacrylates, styrene, and vinyl acetate.[11–17] In contrast, for unsaturated hydrocarbon monomers, only little data are available. A single

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/mren.201900030.

DOI: 10.1002/mren.201900030

PLP-SEC study on butadiene reported k_p values of 57 L mol^{-1} s^{-1} at 30 °C.[18] Further, ethene k_p was derived from high-temperature high-pressure radical polymerizations of ethene applying PLP in conjuction with in-line time-resolved NIR spectroscopy.[19,20] If the data is extrapolated to 20 °C at ambient pressure, a k_p value of 9 L mol^{-1} s^{-1} is obtained, which is rather close to butadiene and the above-mentioned isoprene data.

Previously, it was discussed in detail that the PLP conditions, namely laser pulse repetition rate and photoinitiator concentration, have to be adjusted for each monomer to account for the specific termination rate coefficients of a monomer.[21–24] For example, monomers such as vinyl acetate associated with high termination rate coefficients may need high laser pulse repetition rates and low initiator concentrations to limit the number of termination events between two subsequent laser pulses. Conversely, monomers with low termination rate coefficients require the use of low laser pulse repetition rates and high initiator concentrations. For PLP of isoprene variation of laser pulse repetition rate and initiator concentration to a large degree did not allow for the determination of isoprene homopolymerization k_p at ambient conditions.[8] The origin of this finding may be seen in the very slow polymerization rate. Even though long pulsing times were chosen, only negligible amounts of polyisoprene (PIP) were obtained at ambient conditions. Due to high volatility of isoprene PLP experiments at higher temperatures are not feasible at ambient pressure. In the current study polymerizations were carried out at higher pressure, thus, allowing for higher reaction temperatures and higher k_p. In addition, it is well known that k_p in free radical polymerizations is characterized by a negative activation volume.[24,25] Consequently, elevated pressure leads to an enhancement of k_p, too. Moreover, the termination rate coefficients are decreased at higher pressure.[24,25]

Here, isoprene homopropagation k_p values are reported as a function of temperature and pressure. Thus, estimation of k_p for polymerizations at close to ambient pressure is possible. In addition, data for polymerizations in solution with dimethyl acetamide (DMAc) are reported. A polar solvent was chosen to investigate how a polar substance affects the IP propagation rate coefficients, because in copolymerizations polar (meth) acrylate monomers may be used, which may act as a cosolvent. The data are important for planning and optimizing technical processes as well as for the development of new materials with novel properties.

2. Experimental Section

2.1. Materials

Isoprene (<1000 ppm *p-tert.*-butylcatechol as inhibitor, Sigma–Aldrich) was used as received. The photoinitiator DMPA (2,2-dimethoxy-2-phenylacetophenone, 99%, Sigma–Aldrich), methanol for polymer precipitation (reagent grade, ACP Chemicals Inc.), and the SEC solvent tetrahydrofuran (THF, 99%, Grüssing) were used as received.

2.2. PLP Setup

Low-conversion (<3%) isoprene polymerizations were performed with a pulsed Coherent Xantos XS-500 excimer laser operated at a wavelength of 351 nm (XeF) with 3 to 15 ns pulse duration and a pulse energy of 3 mJ per pulse. The polymerization mixture was prepared with DMPA concentrations of 5 or 10 mmol L^{-1} as indicated in **Table 1**. The mixture was introduced into an optical high-pressure cell equipped with two sapphire windows, which were transparent in the UV and the NIR spectral range, and a thermocouple positioned directly at the reaction volume.[26,27] The optical path length was around 43 mm. A detailed description of the reaction cell is given elsewhere.[26,27] Temperature was monitored during laser pulsing and never increased by more than 0.2 °C. After pulsing, the reaction mixture was expanded into a vial containing methanol. Residual isoprene monomer and methanol were removed under an air stream, the polymer was dissolved in THF (5 mg mL^{-1}), and the solution filtered through a 0.2 µm nylon filter prior to SEC measurement.

2.3. Polymer Characterization

Molar mass distributions were measured by means of size-exluclusion chromatagraphy using a Waters 515 HPLC pump, a Knauer Marathon autosampler, a Knauer Smartline RI detector 2300, and four columns (Polymer Laboratories PLgel 20 µm MIXED-A). The system was operated at 25 °C with a flow rate of 1 mL min^{-1} and THF used as eluent. Calibration was established with polystyrene standards (PSS) ranging from 700 to 2.57 10^6 g mol^{-1}.

Table 1. Activation energy, E_A, activation volumes, $\Delta V^{\#}$, and k_p values for bulk polymerizations at 50 °C and ambient pressure for different types of monomers.

monomer	E_A [kJ mol^{-1}]	A [10^6 L mol^{-1} s^{-1}]	$\Delta V^{\#}$ [cm^3 mol^{-1}]	k_p @ 50°C [L mol^{-1} s^{-1}]
Methyl acrylate	17.3[14]	14.1[14]	−11.2[34]	22 000
Methyl methacrylate	22.4[12]	2.67[12]	−16.7[35]	639
Styrene	32.5[11]	42.7[11]	−11.7[36]	238
Ethene	34.3[19,20]	–[a)]	−27[19,20]	54
Vinylidene fluoride	30.2[33]	466[33]	−22.7[33]	6114
1,3-Butadiene	35.7[18]	80.5[18]	–[b)]	136
Isoprene	40.0[c)]	289[c)]	−19.3[c)]	99

[a)] A not available at ambient pressure; [b)] Not determined; [c)] Taken from linear regression.

2.4. Calculation of Absolute Polymer Molar Masses

From the molar mass distributions determined via SEC calibration with polystyrene (PS) as calibration standard absolute molar masses were calculated according to Equation (2) based on the concept of universal calibration.[28]

$$\log(M_P) = \frac{1}{1+a_P} \cdot \log\left(\frac{K_S}{K_P}\right) + \frac{1+a_S}{1+a_P} \cdot \log(M_S) \quad (2)$$

with the molar mass based on PS calibration, M_s, and the absolute molar mass, M_p, of the polymer of interest. The Mark–Houwink parameters for PS and polyisoprene (PIP) taken from literature are as follows:

PS:[29] $a = 0.716$, $K = 1.14\ 10^{-4}$ dL g^{-1}

PIP:[30] $a = 0.735$, $K = 1.77\ 10^{-4}$ dL g^{-1}

3. Results and Discussion

Recently, PLP-SEC experiments of isoprene were carried out at room temperature. The experiments were not successful for laser pulse repetition rates ranging from 20 and 140 Hz and photoinitiator concentrations from 5 to 10 mmol L^{-1}.[8] The major reason for failure of the experiments was seen in the very slow propagation rate coefficients and the associated very small amount of poly(isoprene) obtained. In order to increase the rate of polymerization in this contribution, pressures ranging from 134 to 1320 bar were applied. In addition to enhancing k_p, the termination rate coefficients were decreased at higher pressure,[25] thus, further increasing the amount of polyisoprene obtained. The first set of PLP experiments was carried out at 75 °C and 350 bar with laser pulse repetition rates ranging from 0.5 to 5 Hz and DMPA concentrations of 5 mmol L^{-1} were used. In all cases sufficient polymer masses were obtained, however, the molar mass distributions (MMDs) were rather monomodal and did not show the typical PLP structure with at least two inflection points on the distribution. The monomodal MMDs suggest that the number of termination events between subsequent laser pulses was too high. As a consequence a correlation between chain length and the time between pulses did not exist. Thus, a second set of experiments was carried out at the same temperature and pressure, but with laser pulse repetition rates of 20, 40, 60, and 80 Hz and initiator concentrations of 5 and 10 mmol L^{-1}. Molar mass distribution showing a typical PLP shape with two inflection points were obtained. The temperature and pressure dependencies of k_p were studied with intermediate pulse repetition rates of 40 and 60 Hz and 5 or 10 mmol L^{-1} DMPA. In addition, some experiments at higher temperatures and pressure were performed with higher pulse repetition rates. The details of every single experiment are provided in Table S1, Supporting Information.

As an example, the upper part of **Figure 1** shows the MMDs obtained at temperatures ranging from 55 to 95 °C. The laser pulse repetition rate was 40 Hz and the DMPA concentration was 5 mmol L^{-1} in all cases. All MMDs show a shoulder or even a second maximum on the high molar mass side of the

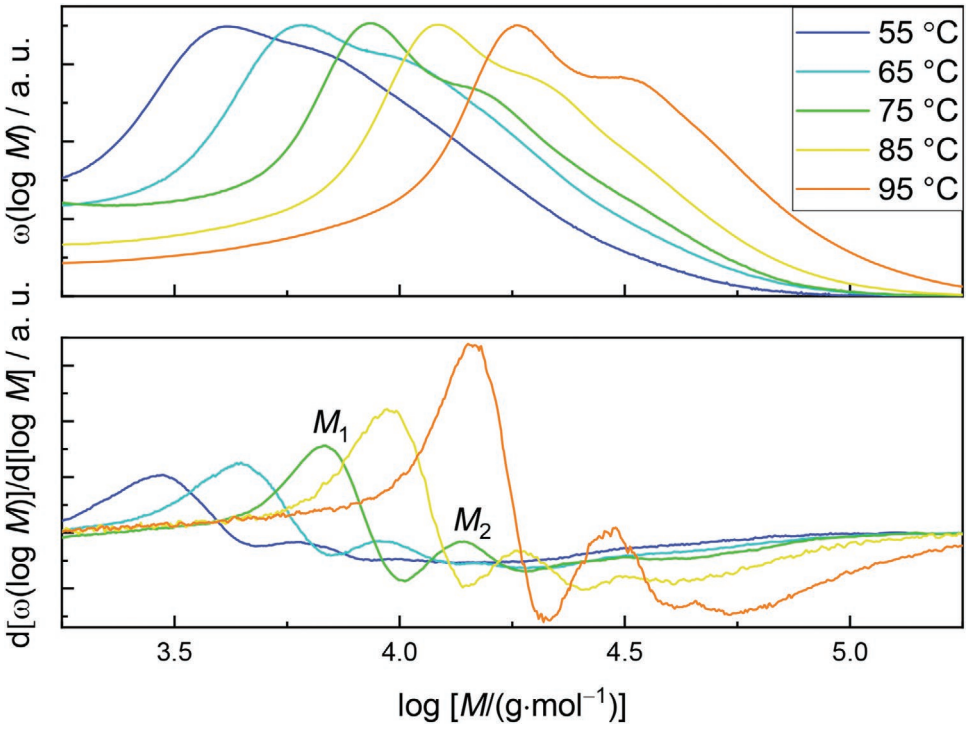

Figure 1. Molar mass distribution (top) and associated first derivative (bottom) obtained from isoprene PLP at temperatures ranging from 55 to 95 °C, 350 bar with a DMPA concentration of 5 mmol L^{-1} at 40 Hz. As an example, the first and second inflection points of the MMD obtained at 75 °C are marked with M_1 and M_2.

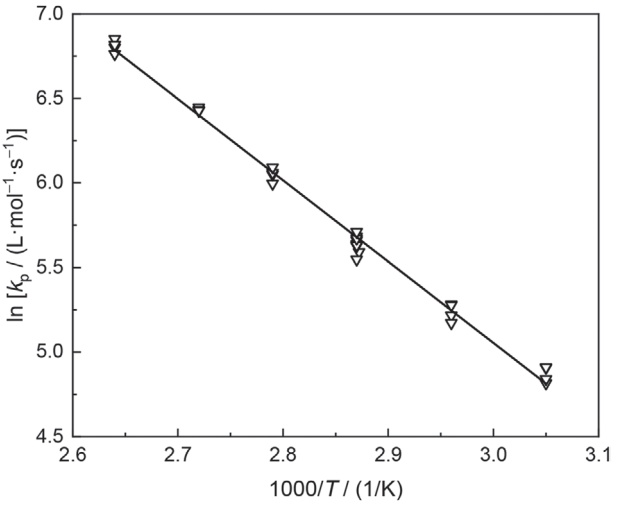

Figure 2. Arrhenius diagram of k_p derived from bulk PLP at 350 bar.

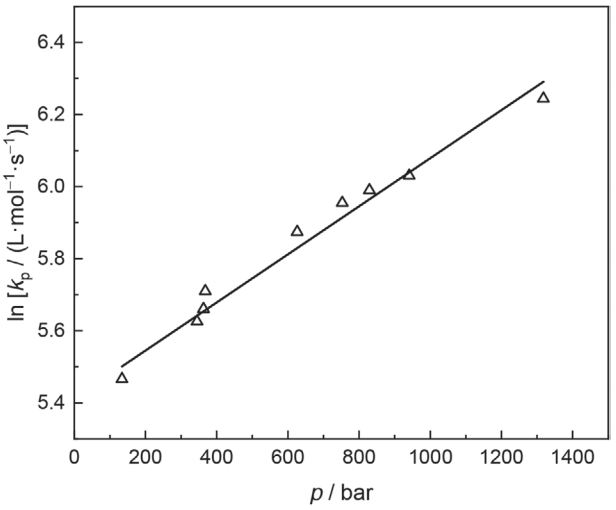

Figure 3. Pressure dependence of k_p for PLP experiments at 75 °C.

distribution, which is typical for successful PLP experiments. In order to identify the characteristic chain length L, which is needed for the calculation of k_p according to Equation (1), the associated first derivative plots are included in the lower part of Figure 1. It is clearly seen that each derivative shows two maxima, indicating the inflection points of the MMDs. As an example, these inflections points are marked with M_1 and M_2 for 75 °C. In all PLP experiments listed in Table S1, Supporting Information, well-structured MMDs comparable to the upper part of Figure 1 were obtained, and in all cases the consistency criterion of $M_1/M_2 \cong 0.5$[21] is fulfilled. **Figure 2** gives the Arrhenius diagram for k_p obtained at around 350 bar. The line was fitted according to

$$\ln k_p = \ln A - E_A/RT \tag{3}$$

with the pre-exponential factor A, activation energy E_A, temperature T, and the gas constant R. Linear regression provides an excellent representation of all experimental data. The Arrhenius parameters of k_p are E_A = (40.0 ± 0.6) kJ mol^{-1} and A = (2.89 +0.71/−0.57) × 10^8 L mol^{-1} s^{-1} for polymerizations at 350 bar. The errors are the SDs obtained via linear regression of the data set.

Generally, isoprene polymerizations are carried out at ambient or slightly elevated pressure, thus, the pressure dependence of isoprene k_p was investigated to determine the activation volume, $\Delta V^{\#}$. The knowledge of $\Delta V^{\#}$ will allow for estimation of k_p at ambient pressure conditions. PLP experiments were carried out at 75 °C and pressures ranging from 134 to 1318 bar. Corresponding MMDs are given as Figure S1, Supporting Information and the full experimental details are provided in Table S1, Supporting Information. The k_p values calculated from M_1 are shown in **Figure 3** as a function of pressure. All data are well represented by the linear relation given in Equation (4):

$$\ln\left[k_p/\left(\text{L mol}^{-1}\ \text{s}^{-1}\right)\right] = 5.41 + \frac{6.67\cdot 10^{-4}\times p}{\text{bar}},\ \text{at } 75\ ^{\circ}\text{C} \tag{4}$$

The activation volume is derived from the slope of the linear relation according to Equation (5)

$$\left(\frac{\mathrm{d}\ln k_p}{\mathrm{d}p}\right)_T = -\frac{\Delta V^{\#}}{\mathrm{R}\cdot T} \tag{5}$$

The associated activation volume is $\Delta V^{\#}$ = −(19.3 ± 1.0) cm^3 mol^{-1}.

To facilitate the estimation of k_p values for polymerizations at ambient pressure conditions an equation for k_p was derived that accounts for the temperature and pressure dependence. Multiple regression analysis according to Equation (6) was carried out. Previously, this equation was successfully applied to describe the temperature and pressure dependence of k_p in styrene, ethene, and vinylidene fluoride homopolymerizations.[31–33]

$$\ln k_p = \ln A - \frac{E_A}{\mathrm{R}\cdot T} - \frac{\Delta V^{\#}\cdot p}{\mathrm{R}\cdot T} \tag{6}$$

with p given in bar and T in K. Fitting of Equation (6) to the experimentally derived k_p data listed in Table S1, Supporting Information was performed using the R Project for Statistical Computing (http://www.r-project.org/). Thirty-nine k_p values listed in Table S1, Supporting Information (represented by y_i in Equation (7)) are provided as vector of dimension 39, the number of experimental data points.

$$y_i = a_0 - a_1\cdot t_{1,i} - a_2\cdot t_{2,i} \text{ with } 1 \le i \le 39 \tag{7}$$

The corresponding information on temperature and pressure are considered with the terms t_1 and t_2 according to Equations (8) and (9):

$$t_{1,i} = \frac{1}{\mathrm{R}\cdot T_i} \tag{8}$$

$$t_{2,i} = \frac{p_i}{\mathrm{R}\cdot T_i} \tag{9}$$

The model coefficients a_0, a_1, and a_2 represent the activation parameters ln$A$, E_a, and $\Delta V^{\ddagger}$, respectively. The following results are obtained: ln[A/(L mol^{-1} s^{-1})] = 19.65 ± 0.18, E_A = (41 200 ± 520) J mol^{-1}, and $\Delta V^{\#} = -(19.1 \pm 0.6)$ cm^3 mol^{-1}. The fit was performed with k_p determined for temperatures ranging from 55 to 105 °C and pressures between 134 and 1318 bar. The parameters and Equation (6) were used to calculate k_p^{model} values at the actual reaction conditions, thus, allowing for comparison with the experimentally derived data, k_p^{exp}. All values are plotted in **Figure 4**. All data points deviate only slightly from the straight line, which corresponds to equal values for ln k_p^{exp} and ln k_p^{model}, and a systematic drift is not seen. Thus, Equation (6) and the parameters given provide an excellent description of the experimental data.

To compare isoprene data with literature data, Table 1 lists activation parameters E_A, A, and $\Delta V^{\#}$ of some typical monomers for radical polymerizations, such as methyl methacrylate (MMA), methyl acrylate (MA), and styrene, together with data for ethene, 1,3 butadiene, and isoprene. It should be kept in mind that the data for MA refers to the propagating chain end radical, because PLP conditions were chosen such that backbiting and associated reactions are negligible. Further details are given elsewhere.[13,14] E_A increases in going from MA to MMA and to styrene. Styrene k_p has the highest activation energy of these three monomers, which may be explained with the resonance stabilized propagating polystyrene radical. The secondary propagating poly(methyl acrylate) radical is less stabilized and k_p has the lowest E_A of all monomers listed. MMA activation energy of k_p is between the values of 17.3 and 32.5 kJ mol^{-1} for MA and styrene k_p, respectively.

Interestingly, the activation energies of ethene, 1,3 butadiene, and isoprene k_p are all higher than E_A of styrene, despite the fact that the propagating radicals are less stabilized than the radicals of the above-mentioned monomers. This fact demonstrates that radical stability is an important but not the only decisive factor affecting propagation rate coefficients. The high E_A and comparably low k_p values for ethene, isoprene, and 1,3 butadiene indicates that monomers with an olefinic double bond, that is not activated by significant inductive or mesomeric effects, is not very reactive. Whether the differences of E_A for isoprene and ethene are significant is beyond the scope of this work. It has to be considered that the activation parameters for ethene were obtained at rather extreme conditions of around 200 °C and 2000 bar with rather modest variation of both parameters, while the isoprene values were obtained not only over a wider temperature and pressure range but also at much lower values of both parameters. Previously, it was shown that E_A of k_p in vinylidene fluoride polymerizations is lowered compared to the ethene value, which was explained by an activation of the double bond due strong electron withdrawal by the fluorine atoms.

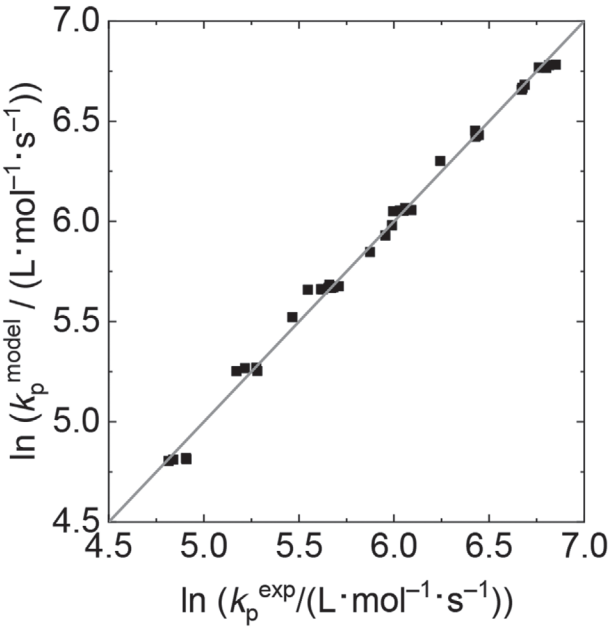

Figure 4. Correlation between predicted, ln k_p^{model} (according to Equation (6) and the parameters given in the text), and experimentally derived, ln k_p^{exp}, propagation rate coefficients.

Fischer and Radom discuss the determining factors for the addition of carbon centered radicals to several alkenes.[37] For the addition of a methyl radical to ethene, an E_A of 31.4 kJ mol^{-1} is reported, which is close to E_A of ethene k_p. Moreover, comparison of E_A for the reaction of a methyl radical with butene or *i*-butene shows a higher value for the nonlinear *i*-butene. Similarly, E_A of isoprene k_p is the highest. Comparison of the pre-exponential A is not as straight forward since A values were reported only for medium pressure gase phase.[37] The trend of significantly increasing A from 1.0×10^8 L mol^{-1} s^{-1} for ethene to 1.6×10^9 L mol^{-1} s^{-1} for vinyl fluoride is in line with the data in Table 1. Moreover, A for the fluorinated alkene is significantly higher than the addition to butene, which resembles the trends observed in Table 1 here. The discussion suggests that the Arrhenius parameters determined for isoprene are in a reasonable range compared to the existing data for other monomers and the addition of small radicals to alkenes.

The activation volumes may be related to the volume of the transition state structure (TST). Previously, similar but different $\Delta V^{\#}(k_p)$ for styrene, acrylates, and methacrylates were explained by the different substitution pattern at the α position of the propagation radicals.[38] This reasoning does not explain why $\Delta V^{\#}$ of ethene and VDF k_p is significantly higher than all other values despite the fact that the least steric hindrance is associated with ethene or VDF propagation. Previously, this finding was explained with the large differences in density of the monomer and polymer for both systems, which are 40% for VDF and 50% for ethene.[33] For the liquid monomers typically the difference is lower, e.g., for methyl methacrylate and its polymer the density difference is around 25%.[39] Following this line, it is reasonable that isoprene k_p is associated with an intermediate value of $\Delta V^{\#}$. At ambient conditions the monomer density is 0.68 g mol^{-1} and the polymer density around 0.91 g mol^{-1}.[40]

Finally, the impact of a solvent on isoprene k_p was investigated, because it is well known that organic solvents may affect k_p in radical polymerizations.[41,42] The majority of investigations into the solvent influence on k_p referred to acrylate and methacrylate type monomers. The strongest solvent influences were reported for water, ionic liquids, or organic solvents such as DMSO, benzyl alcohol, or *N*-methyl pyrrolidinone.[41,42] If

monomer and solvent are rather similar, and if the solvent is a good solvent for the polymer, the solvent influence on k_p is modest. Contrary, information on the solvent influence on k_p for nonpolar monomers is rather scarce. It appeared important to study the solvent influence on isoprene k_p, in particular since in copolymerization systems the comonomers may be considered as a cosolvent, which may affect the propagation kinetics. For this reason, here a solvent was used that should lead to significant interactions between solvent, monomer, and polymer. It was anticipated that dimethyl acetamide (DMAc) fulfills this requirement since it dissolves a very large variety of polymers. The DMAc impact on k_p was investigated at 95 °C and 350 bar using a laser pulse repetition rate of 60 Hz. The monomer concentration c_M was lowered down to 30% of the bulk value, $c_{M,bulk}$. The results are listed in Table S2, Supporting Information, and depicted in **Figure 5**. It is obvious that the propagation rate coefficient is increasing slightly. At the highest dilution k_p is enhanced by around 25% compared to the bulk value. Due to this rather small solvent influence on k_p, we refrained from studying the pressure and temperature impact on the solvent influence, because rather large quantities of chemicals are needed for rather time-consuming PLP experiments at high pressure.

Previous studies on the solvent influence on k_p found a significant variation of E_A only in cases where ionic liquids were used as solvents or where H bonds were formed between the solvent and the monomer moieties.[41] In the absence of such specific interactions, no significant solvent induced change in E_A of k_p was determined. Along this line the modest variation in k_p observed here is not expected to be due to a variation in E_A. It may be discussed whether the findings are caused by a variation of the pre-exponential factor A or a non-ideal mixture of monomer and polymer in the solvent. The latter was discussed for example with respect to the impact of supercritical CO_2 on (meth)acrylate k_p[43,44] or the variation of methacrylate k_p for polymerizations in toluene.[45–47]

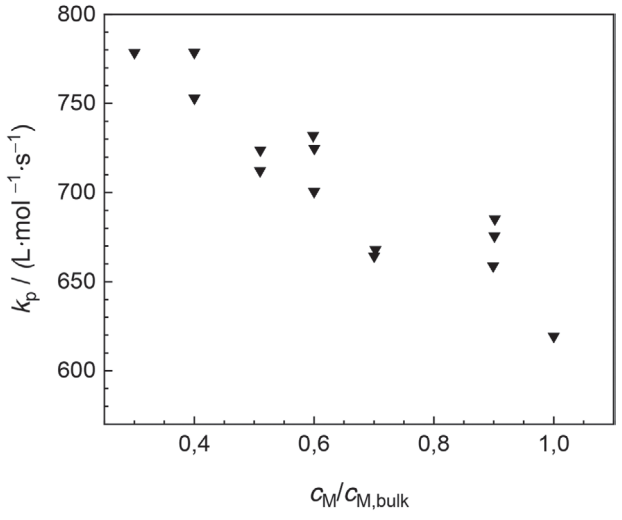

Figure 5. Variation of the apparent propagation rate coefficient, k_p^{app}, as a function of the relative monomer concentration $c_M/c_{M,bulk}$ derived from polymerizations at 95 °C and 350 bar.

Equation (1) indicates that the experimentally accessible quantities L and t allow only for the determination of the product $k_p \cdot c_M$. Thus, data evaluation using the overall monomer concentration in the system will lead to an alteration of the rate coefficient observed in cases, where non-ideal mixing of monomer, polymer, and solvent occurs. For a detailed discussion of this aspect, the reader is referred to the original literature.[35,43,45–47] For the IP/DMAc system, non-ideal mixing and the occurrence of local monomer concentrations or the need for using activities[42] rather than concentrations is also suggested to be the origin of the apparent lowering of k_p. A detailed investigation into the origin of the rather small variations in k_p is beyond the scope of the manuscript. For practical purposes it is important to note that the presence of polar species affects the propagation kinetics only to a small extent. For example, in IP copolymerizations with small amounts of polar monomers the impact due to the comonomers's role of being a cosolvent is suggested to be negligible.

Comparison of the results with literature data is limited since information on the solvent influence on nonpolar monomers is available only for styrene polymerizations.[47–50] In all cases, a modest reduction in k_p by ≤25% was reported, contrary to the enhancement of k_p in the IP/DMAc system. This finding may be due to π–π stacking of the aromatic ring in the polystyrene chains, thus, leading to slightly more dense polymer coils and consequently a slight reduction of the monomer concentration in the vicinity of the propagating chain end. Such a reduction of the local monomer concentration and its impact on the k_p determination was detailed elsewhere.[44,47] In the IP/DMAc system favorable interactions may be seen between DMAc molecules, but not between isoprene moieties and DMAc molecules. Thus, the local isoprene concentration in the vicinity of the chain end may be slightly higher than the overall monomer concentration. In principle, the data can be discussed in terms of the publication by Deglmann et al.,[42] who proposed to used activities rather than local monomer concentrations. The concept comprises using two terms, a combinatorial term accounting for the molar volumes of monomer, solvent, and transition state structure, and a residual term accounting for enthalpic and entropic contributions. However, due to the rather small DMAc influence on IP k_p, due to lack of data for the molar volumes of the solvent at PLP conditions and the fact that the temperature dependence of the solvent influence was not investigated, we refrained from a detailed analysis according to the concept of Deglmann et al.[42]

4. Conclusions

Despite several technical applications of isoprene polymers, only little is known on the kinetics of robust radical polymerizations so far, at least partially being due to low volatility of isoprene and very low propagation rate coefficients. In this contribution, high polymerization pressures and temperatures of up to 105 °C were chosen in order to enhance the polymerization rate. For PLP-SEC experiments, the parameters related to radical concentrations, namely laser pulse repetition rate and photoinitiator concentrations, were optimized with respect to achieving a high probability of chain termination by

the periodically changing radical concentration. Molar mass distributions with a typical PLP-induced shape were obtained that fulfill the consistency criteria put forward by an IUPAC Polymer Division Working Party.[10] The Arrhenius parameters $A = 28.9 \cdot 10^7$ L mol^{-1} s^{-1} and $E_A = 40.0$ kJ mol^{-1} were determined for isoprene k_p at 350 bar. In addition, an activation volume of –19.3 cm^3 mol^{-1} was obtained. A relation for k_p determination as a function of temperature and pressure is reported, which allows for the calculation of k_p at ambient pressure conditions. The activation parameters indicate that non-activated olefinic hydrocarbon monomers are associated with high E_A and rather high A. Moreover, the data are in agreement with model reactions, where methyl radicals were added to several alkenes. Compared to monomers typically used in radical polymerizations the isoprene k_p values are low. For example, at 50 °C isoprene k_p is 99 L mol^{-1} s^{-1}, which is lower than the corresponding values of 238 L mol^{-1} s^{-1} for styrene and 639 L mol^{-1} s^{-1} for methyl methacrylate. Investigations into the impact of a polar solvent on isoprene k_p indicate only a small variation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

kinetics, polyisoprene, pulsed laser initiated polymerization, radical polymerization

Received: August 4, 2019
Revised: September 2, 2019
Published online: September 18, 2019

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